

# Developing More Efficient Fuel Cells Using Computational Methods

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In this project we use a number of state-of-the-art, highly parallelized computational-chemistry tools in order to rationalize the fundamental chemical processes occurring at the atomic level in a fuel cell. This knowledge will enable the optimization of materials properties to develop more efficient and robust fuel-cell designs. First-principles quantum-chemistry techniques and more approximate molecular-mechanics-based methods using empirical potentials are employed in parallel with experimental measurements for validation.

We carried out an extensive computational study of the structure, reactivity, and stability of three different platinum-nickel (Pt-Ni) alloys, Pt<sub>3</sub>Ni, PtNi, and PtNi<sub>3</sub> using the Vienna Ab Initio Simulation Package (VASP) [1], a periodic density functional theory code. Our aim was to determine the effect of the subsurface layer composition on the catalytic activity of the platinum surface. These alloys are candidates for the replacement of pure platinum electrodes in fuel cells used to convert hydrogen and oxygen fuel to water and electricity [2]. Since pure platinum electrodes are costly, one method for alleviating this cost is to alloy platinum with base metals, such as nickel. The research question is how this alloying process will impact activity—this computational study attempts to answer this question.

We constructed models for the alloy materials that featured surfaces to which the molecules taking part in the chemical reactions could bind. The surface models featured three types of slabs of platinum and nickel containing a platinum surface monolayer supported on a second layer containing 50%, 100%, and 75% of nickel, respectively, with a bulk layer below to represent alloys with different concentrations of platinum.

Equilibrium adsorption potentials represent the strength of binding of the molecules to the surface. We calculated these potentials for the oxygen reduction reaction (ORR) intermediates—this is the fundamental chemical step in the fuel-cell chemistry that controls the reaction rate and, therefore,

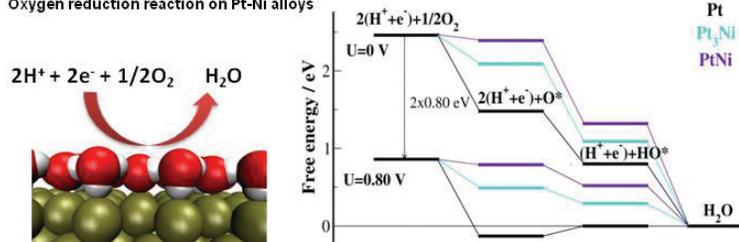
the efficiency of the fuel cell process at the surface. The results of these calculations provide a method for constructing free-energy diagrams for the ORR mechanism and for gauging catalytic activity (Fig. 1).

We also addressed the critical question of the stability of these materials in an aqueous environment. This provides an indication of the lifetime of the fuel-cell materials in a working device. The calculations identify the most stable state of the surface as a function of pH and potential, which reflects the working conditions of a fuel cell. The (111) surface of all three models of Pt-Ni alloys exhibits improved oxygen reduction activity compared with that of pure Pt (111). Our calculations show that the ORR over-potential, which is a measure of the fuel-cell efficiency, decreases in the order Pt (0.55 V) > Pt<sub>3</sub>Ni (0.24 V) > PtNi<sub>3</sub> (0.19 V) > PtNi (0.15 V) [3]. We therefore conclude that the catalytic activity for ORR will increase as Pt < Pt<sub>3</sub>Ni < PtNi<sub>3</sub> < PtNi, and find that the largest improvement occurs for a PtNi alloy with 100% nickel in the second layer. We also predict that PtNi is the least susceptible to corrosion at similar pH and cell potentials based on the calculated shifts of the electrochemical dissolution potentials for the Pt-Ni alloys relative to platinum with values of -0.27 V for PtNi<sub>3</sub>, +0.13 V for Pt<sub>3</sub>Ni, and +0.30 V for PtNi [3].

In addition to this work on bulk metallic structures, we are also investigating the structure and properties of platinum nanotubes as another method of reducing platinum content [4]. We have calculated the relative stability of a large number of platinum (n,m) nanotubes ranging in diameter from 0.3 to 2.0 nm in the gas phase and water environment (Fig. 2). We have also calculated the adsorption energies of intermediates in the ORR (oxygen and hydroxyl) and used them to

Fig. 1. Oxygen reduction reaction on Pt-Ni alloys.

Oxygen reduction reaction on Pt-Ni alloys



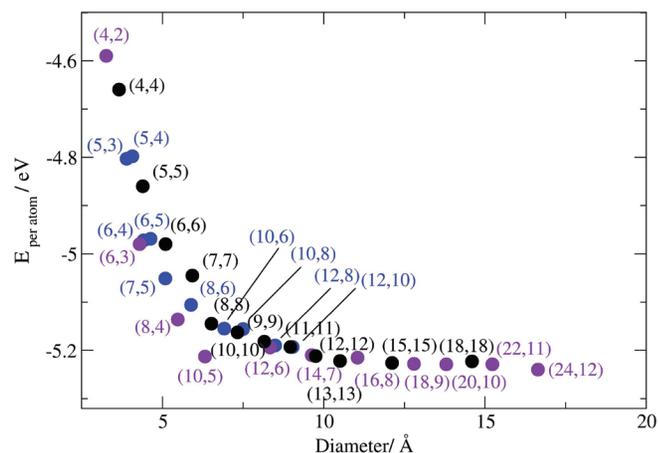


Fig. 2. Calculated stability of platinum nanotubes as a function of diameter.

construct free-energy diagrams for the oxygen reduction dissociation mechanism. Based on these calculations we conclude that the smaller Pt nanotubes (~0.5 nm in diameter) have a huge over-potential for ORR and thus prove to be very poor catalysts for ORR. However, bigger Pt tubes (>1 nm in diameter) have a lower over-potential than bulk platinum for up to 150 meV, indicating that these materials might be better ORR catalysts than bulk Pt.

The stability of the platinum nanotubes in the gas phase is investigated in terms of cell potentials at which the tube will start to dissolve electrochemically. The most stable state of the nanotubes as a function of pH and potential is addressed by calculating its Pourbaix diagrams (Fig. 3). Tubes with  $n=m$  chirality and diameter >1 nm have been shown to endure the highest cell potentials; however, these are still for a 130-meV lower than the cell potentials at which bulk platinum will start to dissolve. In conclusion, we predict that some platinum nanotubes show improved catalytic activity compared to bulk platinum, but they may be more susceptible to corrosion.

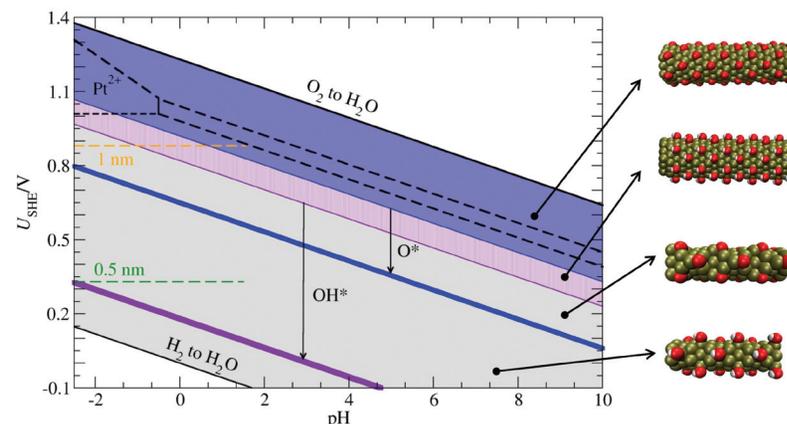


Fig. 3. Pourbaix diagram of platinum nanotubes compared to the bulk (black dashed lines). The regions of oxygen and hydroxide surface adsorptions are shown in blue and violet. The green (orange) dashed lines show the solubility boundary for Pt nanotubes with diameters of 0.5 and 1 nm.

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